Superlattices and Microstructures xxx (2015) 1–8

Contents lists available at ScienceDirect

Superlattices and Microstructures

journal homepage: www.elsevier.com/locate/superlattices

Effect of copper doping on the photocatalytic activity of ZnO thin films prepared by sol–gel method

T. Saidani [a, *], M. Zaabat [a], M.S. Aida [b], B. Boudine [c]

[a] Laboratory of Active Components and Materials, University Larbi Ben M'hidi Oum El Bouaghi, 04000, Algeria
[b] Laboratory of Thin Films and Interface, University of Constantine, Constantine 25000, Algeria
[c] Laboratory of Crystallography, Department of Physics, University of Constantine, Road Ain El bey, 25000, Algeria

ARTICLE INFO

Article history:
Received 16 September 2015
Accepted 21 September 2015
Available online xxx

Keywords:
Cu doped ZnO
ZnO thin films
Sol gel method
Photocatalytic activity

ABSTRACT

In the present work, we prepared undoped and copper doped ZnO thin films by the sol–gel dip coating method on glass substrates from zinc acetate dissolved in a solution of ethanol. The objective of our work is to study the effect of Cu doping with different concentrations on structural, morphological, optical properties and photocatalytic activity of ZnO thin films. For this purpose, we have used XRD to study the structural properties, and AFM to determine the morphology of the surface of the ZnO thin films. The optical properties and the photocatalytic degradation of the films were examined by UV–visibles spectrophotometer. The Tauc method was used to estimate the optical band gap. The XRD spectra indicated that the films have an hexagonal wurtzite structure, which gradually deteriorated with increasing Cu concentration. The results showed that the incorporation of Cu decreases the crystallite size. The AFM study showed that an increase of the concentration of Cu causes the decrease of the surface roughness, which passes from 20.2 for Un-doped ZnO to 12.16 nm for doped ZnO 5 wt% Cu. Optical measurements have shown that all the deposited films show good optical transmittance (77%–92%) in the visible region and increases the optical gap with increasing Cu concentration. The presence of copper from 1% to 5 wt% in the ZnO thin films is found to decelerate the photocatalytic process.

1. Introduction

Nowadays, the researchers give great importance to eliminate the toxic chemical compounds which pollute the environment. Therefore, it is given a great importance to the development of some of the ways that work to convert the toxic organic pollutants into simple harmless elements to eliminate the pollution of the environment. The photocatalytic activity is among the effective methods that have proven their efficiency in this area. A number of photocatalysts have been studied until now such as CdS, TiO_2, Fe_2O_3 and ZnO. ZnO is one of the most studied materials because of its excellent photocatalytic efficiency and good stability.

Zinc oxide (ZnO) is a semiconductor photocatalyst with a wide direct band gap of 3.36 eV and a relatively higher exciton binding energy of 60 meV at room temperature [1]. Because of their physical, optical and electrical

* Corresponding author.
E-mail address: tarek.saidani23@gmail.com (T. Saidani).

http://dx.doi.org/10.1016/j.spmi.2015.09.029
0749-6036/

properties, ZnO thin films have elicited much interest for applications in optoelectronic such as gases sensors, light emitting diodes (LEDs), transistors, solar cells, ultraviolet nanolaser, piezoelectric materials [2–5] and nanodevices [6–13]. Numerous techniques have been used for depositing ZnO thin films. Some of them are pulsed laser deposition (PLD) [14,15], spray pyrolysis [16], reactive magnetron sputtering [17,18], chemical vapor deposition (CVD) [19], Molecular beam epitaxy [20] and the sol–gel method [21] are widely used. Among these techniques, the sol–gel method attracts much attention due to some unique advantage, since it enables to develop low cost, simple deposition equipment, easy adjusting composition and dopants, excellent uniformity, fabricating large area films and low crystallization temperature [22,23].

ZnO thin films with different Cu doping contents were deposited onto glass substrates using sol–gel dip coating method. The main goal of this work is to investigate the role of Cu on structural, morphological, optical properties and photocatalytic activity of ZnO thin films.

2. Experimental

2.1. Preparation of ZnO thin films

Cu doped ZnO thin films were deposited on glass substrate by sol–gel method using dip coating technique. Zinc acetate dihydrate ($Zn(CH_3COO)_2$; $2H_2O$), copper acetate ($Cu(CH_3COO)_2$), ethanol and monoéthanolamine (MEA) ($NH_2CH_2CH_2$–OH) were used as starting material, dopant, solvent and stabilizer, respectively.

ZnO precursor containing Cu-dopants were prepared with different percents (1, 3 and 5wt %), the concentrations were 0.2 mol/L for zinc acetate. Zinc acetate dihydrate and copper acetate were dissolved in ethanol, and then the monoéthanolamine was added to the solution as the stabilizer.

The resulting mixture solution was stirred for 2 h at 333 K by a magnetic stirrer to yield homogeneous solution. The glass substrates were cleaned in acetone, methanol and deionized water, successively. The layers were prepared by dip coating technique with withdrawal speed of 100 mm, each deposited layer was dried at a temperature of 200 °C for 10 min, and finally, the films were annealed at 500 °C for 2 h.

2.2. Characterization

To study films properties, various characterization techniques were used. The X-ray diffraction (XRD, Bruker AXS-8D) with Cu Kα radiation (Cu Kα = 0.154 nm) to study the structural properties, films morphology was also characterized by atomic force microscopy (A100-AFM), optical properties was determined using spectrophotometer (Jasko V-630) in the wavelength range 300–1100 nm.

2.3. Photocatalytic activity

The photocatalytic activity of undoped and Cu doped ZnO thin films was investigated by means of the degradation of orange II (OII) in aqueous solution under visible light at room temperature. Blue light lamp was used as UV source. The photocatalytic degradation was determined by measuring the absorbance of OII solution for every 30 min for 240 min using UV–vis spectrophotometer (Jasko V-630) in the wavelength range 300–800 nm end the degradation efficiency of OII can be calculated by the formula

$$Degradation(\%) = \frac{C_0 - C_t}{C_0} \times 100 = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

where C_0 is the initial concentration, C_t is the concentration after 't' min. A is the initial absorbance and A_t is the absorbance after 't' min.

3. Results and discussions

3.1. Structural properties

The XRD patterns of Cu doped ZnO thin films with different Cu concentration were shown in Fig. 1. As can be seen, seven pronounced diffraction peaks corresponding to (100), (002), (101), (102), (110), (103) and (112) planes of the ZnO are present in all spectra. This result allows to assert that all films have a well polycrystalline nature and hexagonal wurtzite structure with preferential orientation (002), Increasing Cu doping induces films crystallinity deteriorated. No secondary phases related to Cu or CuO phases were observed, indicating that Cu doping did not change the wurtzite ZnO structure, and that Cu^{+2} substituted into the ZnO sites.

The crystallite size and the full width at half maximum (FWHM) of the films were calculated from the XRD data by using Scherer's formula [24]:

Please cite this article in press as: T. Saidani et al., Effect of copper doping on the photocatalytic activity of ZnO thin films prepared by sol–gel method, Superlattices and Microstructures (2015), http://dx.doi.org/10.1016/j.spmi.2015.09.029

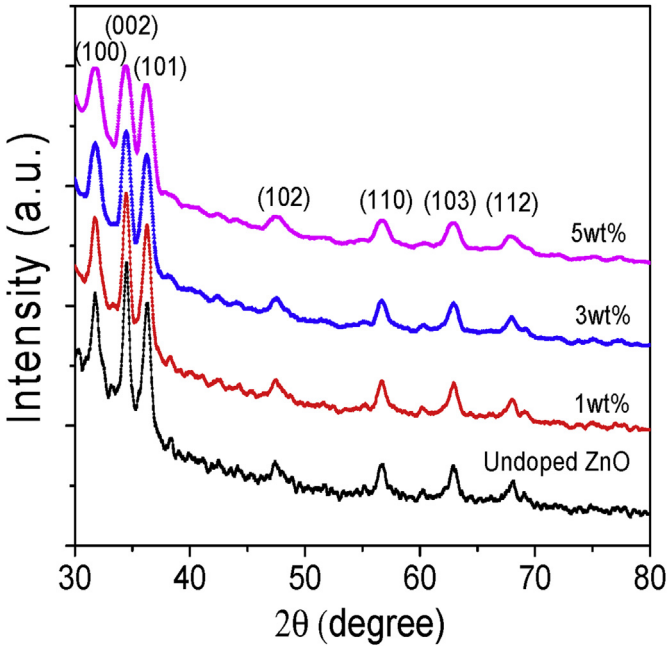

Fig. 1. XRD patterns of ZnO thin films with various Cu doping concentrations.

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{2}$$

where λ is the X-ray wavelength, β is the full width at half maximum of the XRD peak, θ is the Bragg diffraction angle. This extracted data are plotted in Fig. 2. From this curve, it is clearly seen that FWHM increased with Cu incorporation. This indicates the degradation of film crystallinity, This is due to the influence of stresses arising from the differences in ionic radii between of the host material Zn^{+2} (0.0074) and the dopant Cu^{+2} (0.0073) [25].

The XRD analysis revealed that the calculated crystallite size is between 14.97 and 7.63 nm. As shown in Fig. 2 the crystallite size decreases with increasing in the Cu doping, indicating that Cu^{+2} substitute into the Zn^{+2} or incorporate into interstitial sites in the lattice of ZnO. These results indicate that the crystallinity of the ZnO film deteriorates with increasing Cu doping concentrations.

3.2. Surface morphological

The surface morphologies of the ZnO thin films with different Cu doping concentrations were examined by the atomic force microscope. Our results are displayed in Fig. 3. All films surface were highly dense and without any cracks. On close inspection of the AFM images, it was noticed that the grain size of the films decreased with an increase in Cu doping concentration, which passes from 31.5 for pure ZnO to 19.07 nm for doped ZnO 5 wt% Cu, indicating that appropriate Cu doping content could decrease the surface morphology of ZnO thin films. This result is in agreement with the analysis of XRD.

From the AFM measurements the root mean square (RMS) surface roughness of Cu doped ZnO thin film with different Cu doping concentration can be obtained and plotted in Fig. 4. Note that by the increasing of Cu doping concentration, the surface roughness is decreased from 20.2 to about 12.16 nm from un-doped film to doped by 5 wt%. This was attributed to the decrease of grain size which resulted in a decrease in surface roughness.

3.3. Optical properties

The transmittance spectra of the ZnO thin films with different Cu doping concentrations were measured as a function of wavelength in the range of 300–1100 nm and illustrated in Fig. 5. It can be observed that all the films exhibit a high optical transmittance (>77%) in the visible region, As can be seen, the transmittance increased from 77% to 92% when the concentration of Cu was increased from un-doped film to doped by 5 wt%, In doping reason, copper atoms occupy vacant sites ZnO and reduce dispersion of light, leading to the increase of the transmittance.

The band gap Eg values of the ZnO thin films with different Cu doping concentrations was obtained using Tauc's equations [26]:

Please cite this article in press as: T. Saidani et al., Effect of copper doping on the photocatalytic activity of ZnO thin films prepared by sol–gel method, Superlattices and Microstructures (2015), http://dx.doi.org/10.1016/j.spmi.2015.09.029

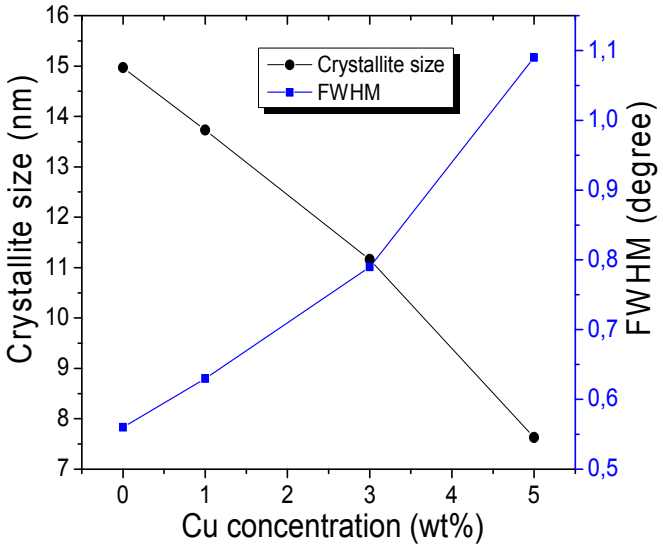

Fig. 2. FWHM of the main XRD peak and corresponding crystallite size of ZnO films as a function of Cu doping concentrations.

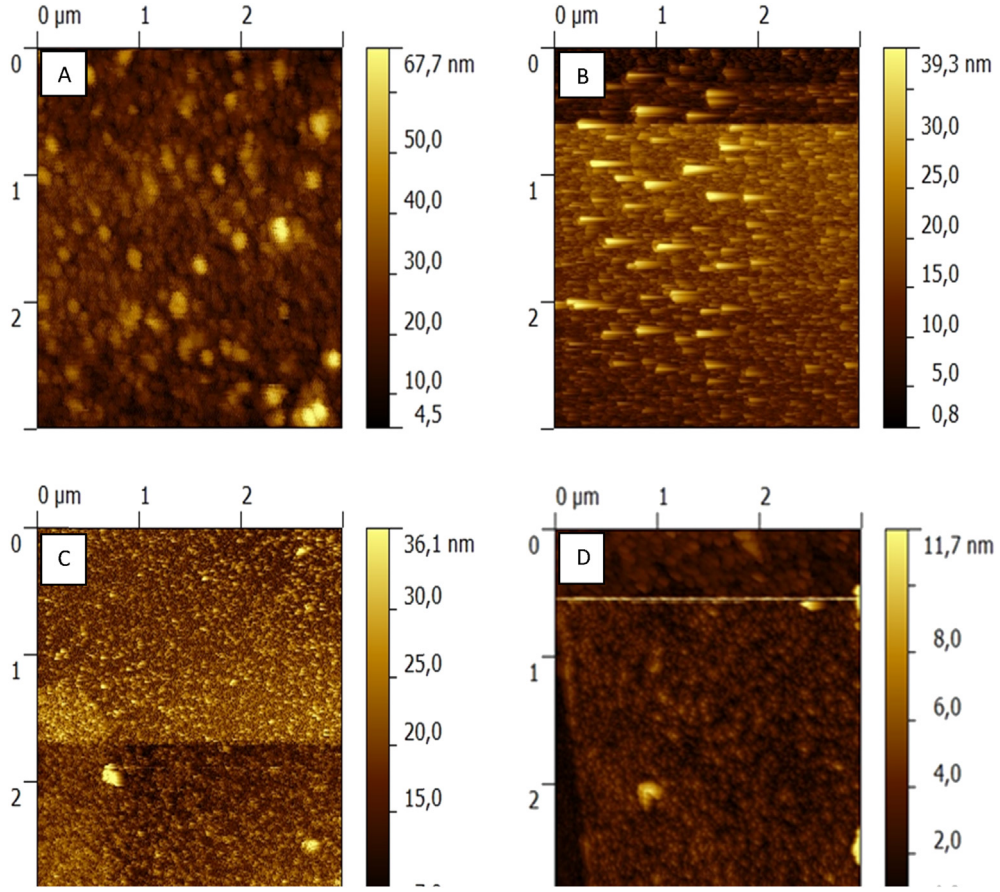

Fig. 3. Surface morphologies of ZnO thin films with various Cu doping concentrations (A) 0 wt%, (B) 1 wt%, (C) 3 wt% and (D) 5 wt%.

Please cite this article in press as: T. Saidani et al., Effect of copper doping on the photocatalytic activity of ZnO thin films prepared by sol–gel method, Superlattices and Microstructures (2015), http://dx.doi.org/10.1016/j.spmi.2015.09.029

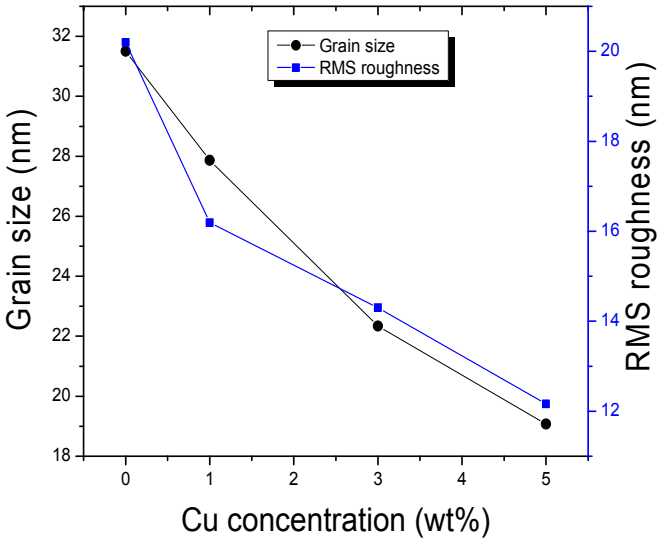

Fig. 4. Variation of grain size and RMS roughness of ZnO thin films as a function Cu doping concentrations.

$$\alpha h\upsilon = A(h\upsilon - E_g)^{1/2} \tag{3}$$

where hυ is the photon energy of the incident photons, A is a constant, and α is the absorption coefficient. The absorption coefficient (α) can be determined from the transmittance of the films with the formula $\alpha = (1/d)\ \ln\ (1/T)$, where d is the thickness of the films and T is the transmittance.

Fig. 6 shows the relationships between $(\alpha h\upsilon)^2$ and photon energy (hυ) for undoped and Cu doped ZnO. The value of the energy gap can be determined by the extrapolation of the linear region of the curve $(\alpha h\upsilon)^2$ versus photon energy (hυ) on the x-axis. The optical band gap, as a function of Cu concentrations, is shown in the inset of Fig. 7. It is clearly seen from Fig. 7, that the optical gap of ZnO thin films is increased from 3.34 to 3.38 eV when the Cu concentration was increased from 0 to 5 wt%. This broadening of the band gap for Cu doped ZnO thin films may be attributed to the increase in free electron concentration in ZnO thin films because of the substitution of the Cu ion into Zn sites, the Fermi level shifts up into the conduction band, this increase in the concentration of free electrons blocks lower states in the conduction band and the Fermi level shifts up into the conduction band, This is consistent with the Burstein-Moss theory [27,28].

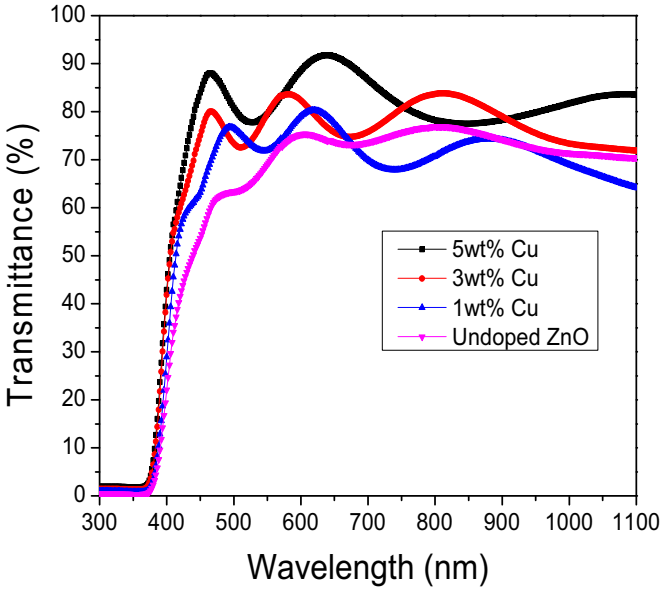

Fig. 5. Transmittance spectra of ZnO thin films with various Cu doping concentrations.

Please cite this article in press as: T. Saidani et al., Effect of copper doping on the photocatalytic activity of ZnO thin films prepared by sol–gel method, Superlattices and Microstructures (2015), http://dx.doi.org/10.1016/j.spmi.2015.09.029

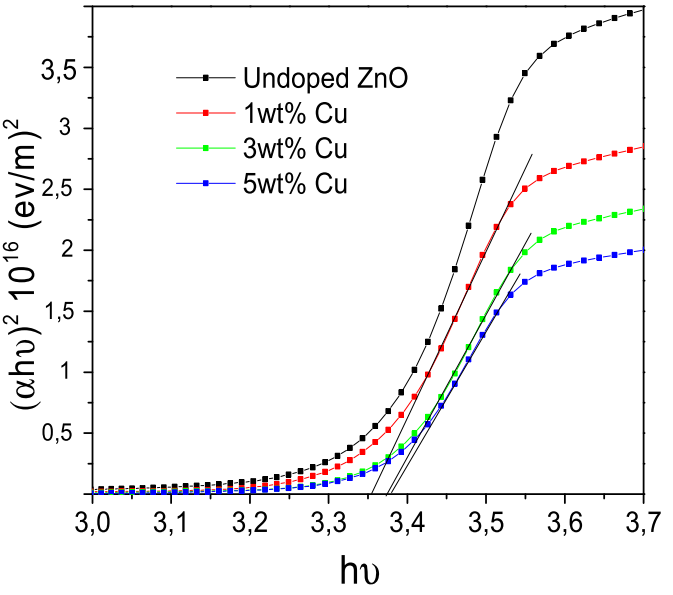

Fig. 6. Plot of $(\alpha h\upsilon)^{1/2}$ versus $(h\upsilon)$ of the ZnO thin films with different Cu doping concentrations.

3.4. Photocatalytic activity

The photocatalytic activity of un-doped and Cu doped ZnO thin films was studied by the degradation of orange II (OII) solution to visible light at room temperature. This study was conducted in the presence and in the absence of ZnO thin films.

Fig. 8(a) shows the effect of Cu doping with different concentrations on the photocatalytic degradation of orange II solution under visible light. As can be seen from Fig. 8(a) there is no degradation of orange II in the absence of ZnO thin films. However with the presence of ZnO thin films we observe a maximum degradation for the films of undoped ZnO. With the increase of copper concentration in the ZnO thin films, the degradation of orange II decreases. This was attributed to the decrease of surface roughness which resulted in a deceleration of the photocatalytic process.

The relationship between the degradation and time of un-dopped and Cu doped ZnO thin films for an irradiation time of 240 min is illustrated in Fig. 8(b). From these curves, it is evident that the degradation efficiency decreases to be 72%, 70.3%,

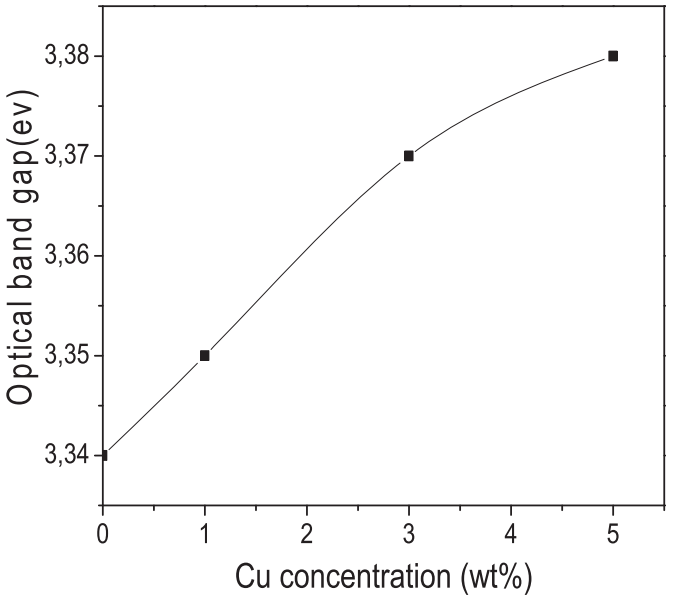

Fig. 7. Variation of optical band gap as a function of Cu doping concentration.

Please cite this article in press as: T. Saidani et al., Effect of copper doping on the photocatalytic activity of ZnO thin films prepared by sol–gel method, Superlattices and Microstructures (2015), http://dx.doi.org/10.1016/j.spmi.2015.09.029

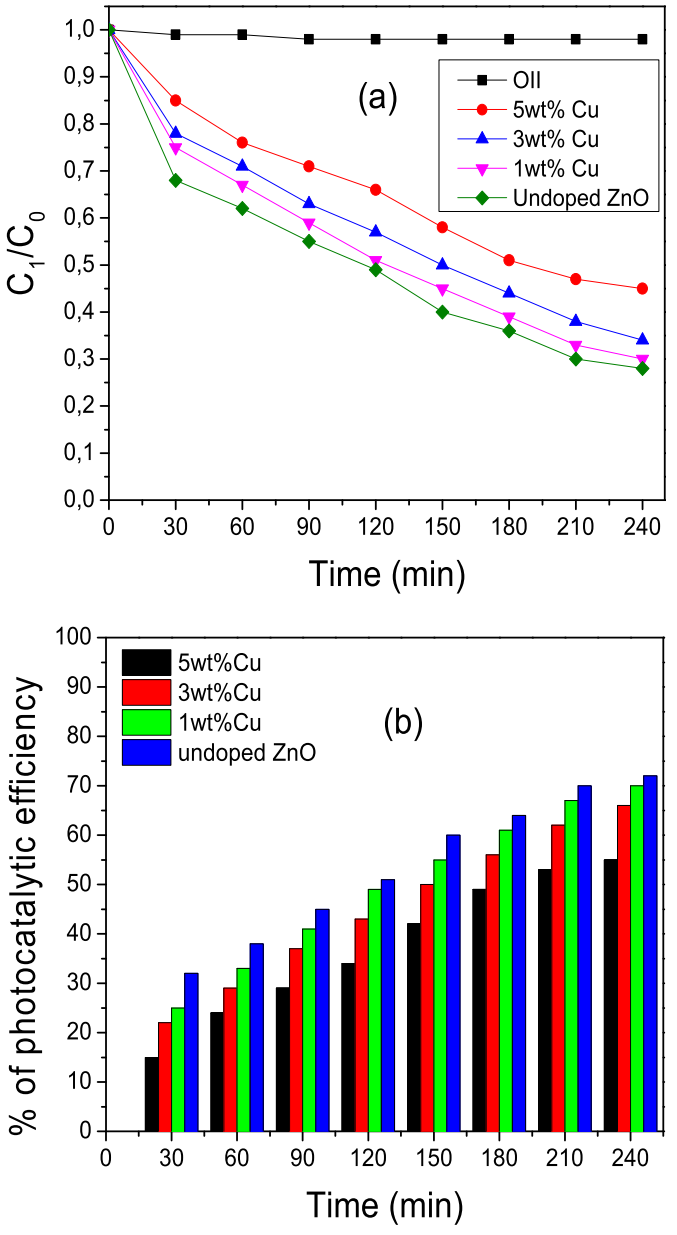

Fig. 8. Photocatalytic (a) degradation and (b) degradation efficiency of OII for undoped and Cu doped ZnO thin films.

66.8% and 55.3% with increasing the Cu concentrations 0, 1, 3 and 5 wt% respectively. It is clearly seen that the photocatalytic process decelerated with an increase in the Cu concentrations.

4. Conclusions

The Cu doped ZnO thin films were deposited by sol–gel method on glass substrates. The effect of copper doping with different concentrations on the structural, morphological, optical properties and photocatalytic activity of the films was investigated. The X-ray diffraction reveals that all films had a polycrystalline nature and hexagonal wurtzite structure with preferential orientation (002), which gradually deteriorated with increasing the Cu concentration. The results showed that the incorporation of Cu decreases the crystallite size. The AFM study revealed that the increase of the concentration of Cu causes the reduced surface roughness, which passes from 20.2 for Un-doped ZnO to 12.16 nm for doped ZnO 5 wt% Cu. Optical measurements have shown that all the deposited layers showed high transmittance which is greater than 77% in the visible region as well as increasing the optical gap with increasing Cu concentration. The presence of copper from 1% to 5 wt% in the ZnO thin films decelerates the photocatalytic process.

Please cite this article in press as: T. Saidani et al., Effect of copper doping on the photocatalytic activity of ZnO thin films prepared by sol–gel method, Superlattices and Microstructures (2015), http://dx.doi.org/10.1016/j.spmi.2015.09.029

Acknowledgments

This work has been supported by the Laboratory of active components and materials University Larbi Ben M'hidi Oum El Bouaghi, Algeria. We would like to thank Pr. Nadir Bouarissa for assistance with the English.

References

[1] F. Benharrats, K. Zitouni, A. Kadri, B. Gil, Superlattices Microstruct. 47 (2010) 592–596.
[2] Daoli Zhang, Jianbing Zhang, Zhe Guo, Xiangshui Miao, J. Alloys Comp. 509 (2011) 5962.
[3] Seval Aksoy, Yasemin Caglar, Saliha Ilican, Mujdat Caglar, J. Alloys Comp. 512 (2012) 171.
[4] I.Y. Erdogan, O. Gullu, J. Alloys Comp. 492 (2010) 378.
[5] A.I. Inamdar, A.C. Sonavane, S.K. Sharma, Hyunsik Im, P.S. Patil, J. Alloys Comp. 495 (2010), 76 81.
[6] J. Karamdel, C.F. Dee, K.G. Saw, B. Varghese, C.H. Sow, I. Ahmad, B.Y. Majlis, J. Alloys Comp. 512 (2012) 68.
[7] Ibrahim Y. Erdogan, J. Alloys Comp. 502 (2010) 445.
[8] Trilochan Sahoo, Myoung Kim, Mi-Hee Lee, Lee-Woon Jang, Ju-Won Jeon, Joon Seop Kwak, In-Yong Ko, In-Hwan Lee, J. Alloys Comp. 491 (2010) 308.
[9] Chien-Yie Tsay, Kai-Shiung Fan, Sih-Han Chen, Chia-Hao Tsai, J. Alloys Comp. 495 (2010) 126.
[10] B. Kulyk, B. Sahraoui, V. Figa, B. Turko, V. Rudyk, V. Kapustianyk, J. Alloys Comp. 481 (2009) 819.
[11] C.D. Lokhande, A.M. More, J.L. Gunjakar, J. Alloys Comp. 486 (2009) 570.
[12] A.D. Acharya, Shweta Moghe, Richa Panda, S.B. Shrivastava, Mohan Gangrade, T. Shripathi, D.M. Phasec, V. Ganesan, J. Mol. Struct. 1022 (2012) 8.
[13] S.S. Shinde, PrakashS. Patil, R.S. Gaikwad, R.S. Mane, B.N. Pawar, K.Y. Rajpure, J. Alloys Comp. 503 (2010) 416.
[14] A.I. Savchuk, V.I. Fediv, S.A. Savchuk, A. Perrone, Superlattices Microstruct. 38 (2005) 421.
[15] Chien-Yie Tsay, Kai-Shiung Fan, Chien-Ming Lei, J. Alloys Comp. 512 (2012) 216.
[16] Y. Caglar, S. Aksoy, S. Ilican, M. Caglar, Superlattices Microstruct. 46 (2009) 469.
[17] L.P. Peng, L. Fang, X.F. Yang, Y.J. Li, Q.L. Huang, F. Wu, C.Y. Kong, J. Alloys Comp. 484 (2009) 575.
[18] X.C. Wang, X.M. Chen, B.H. Yang, J. Alloys Comp. 488 (2009) 232.
[19] Guangyao Zhu, Gu Shulin, Shunming Zhu, Shimin Huang, Gu Ran, Jiandong Ye, Youdou Zheng, J. Cryst. Growth 349 (2012) 6.
[20] S.J. Jiao, Y.M. Lu, D.Z. Shen, Z.Z. Zhang, B.H. Li, ZhH. Zheng, B. Yao, J.Y. Zhang, D. Zhao, X.W. Fan, J. Luminescence 122–123 (2007) 368.
[21] Seval Aksay, Yasemin Caglar, Saliha Ilican, Mujdat Caglar, Superlattices Microstruct. 50 (2011) 470.
[22] H.E. Camurlu, O. Kesmez, E. Burunkaya, N. Kiraz, Z. Yesil, M. Asilturk, E. Arpac, Chem. Pap. 66 (2012) 461.
[23] L. Malfatti, P. Innocenzi, J. Sol–Gel Sci. Technol. 60 (2011) 226.
[24] R. Anandhi, R. Mohan, K. Swaminathan, K. Ravichandran, Superlattices Microstruct. 51 (2012) 680.
[25] J. Nishino, S. Ohshio, K. Kamata, J. Am. Ceram. Soc. 75 (1992) 3469.
[26] S. Major, A. Banerjee, K.L. Chopra, K.C. Nagpal, Thin Solid Films 143 (1986) 19.
[27] E. Burstein, Phys. Rev. 93 (1954) 632.
[28] T.S. Moss, Phys. Soc. Lond. B 67 (1954) 775.

Please cite this article in press as: T. Saidani et al., Effect of copper doping on the photocatalytic activity of ZnO thin films prepared by sol–gel method, Superlattices and Microstructures (2015), http://dx.doi.org/10.1016/j.spmi.2015.09.029